DISSOLVED PHOSPHORUS DYNAMICS IN SHALLOW GROUNDWATER

A Thesis

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Master of Science

by

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ABSTRACT

Dissolved phosphorus (P) reaching streams and lakes from agricultural areas is a persistent problem that impacts water quality and aquatic ecosystems downstream; one cause of this is a lack of understanding of how P is released from the soils of riparian and other hydrologically active areas. We monitored shallow groundwater and surface water for a year in three periodically water-saturated areas near an agricultural field in Cortland County, NY. P concentrations followed a seasonal pattern in all three sites, with organic P peaking in the summer, and inorganic P highest in the fall. The forested upland site had persistently higher concentrations of P, iron and dissolved organic carbon in its shallow groundwater than the two riparian sites also monitored in this study. The upland site also differed from the lowland sites in that it became saturated throughout the year after precipitation or snow melts, but drained relatively quickly. In contrast, the two riparian sites were seasonally saturated. This study suggests that position in landscape might be as important as land use in controlling P solubilization.

BIOGRAPHICAL SKETCH

Josephine Archibald was born in the UK, but spent most of her childhood in New Rochelle NY with her parents and four siblings. She graduated from Oberlin College in 2003 with a degree in Biology, Environmental Studies and a minor in Math. In June 2004, Josephine became an Environmental Education Peace Corps volunteer in Morocco. She lived there for two years, helping a small shepherding community improve their access to clean water and coordinating environmental and health education.

Josephine's experience in Morocco motivated her to gain some more technical knowledge and apply to graduate school in environmental engineering. She immediately fell in love with Ithaca once upon arrival, and enjoys all the outdoor concerts, festivals and other community events that are so plentiful here. In addition, she can frequently be found cross-country skiing when there's enough snow, and kayaking or swimming in Cayuga Lake in the summer.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Todd Walter, for his continual support.

Also, thanks to

- Beth Boisvert, who collected many of the samples in early 2008, and kept the piezometers in working order.
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LIST OF ABBREVIATIONS

P - Phosphorus

SRP – Soluble Reactive Phosphorus, generally assumed to be the inorganic fraction of dissolved P

Tot P – Total Dissolved Phosphorus in a water sample

DOC – Dissolved Organic Carbon

VSA – Variable Source Areas, or areas of the land that saturated frequently, and therefore contribute a large amount of runoff to downstream water bodies.

WR - Wet Riparian Site

DR - Dry Riparian Site

UF – Upland Forested Site

STI – Soil Topographic Index, determined by contributing area, transmissivity of the soil, and slope. Generally, values greater than 8 suggest a high probability of water-saturation.

Water Saturated – In this study, we assumed a site was saturated when the water table was within 10 cm of the soil surface (or above the soil surface)

CHAPTER 1

INTRODUCTION

Excess phosphorus (P) is widely acknowledged to be the main cause of eutrophication in fresh water bodies throughout the world, with manure-fertilized agriculture a major non-point source of this pollution (Carpenter et al. 1998; Vollenweider 1968). Because the majority of phosphorus that reaches streams and lakes is bound to soil, many efforts to prevent freshwater eutrophication focus on soil conservation and overland runoff control (Sims et al. 1998). However, best management practices (BMPs) aimed at soil conservation such as vegetative buffer strips that catch sediment and cover crops which prevent soil erosion are not always effective at preventing P pollution (Dorioz et al. 2006). Instead, researchers are finding that soluble reactive P (SRP) and other dissolved forms of P, which are more ecologically available, can have a disproportionately large environmental impact, and that soil conservation alone will not prevent SRP transport (Walter et al. 1979). Thus it is important to understand the processes that are involved in solubilizing P from soil and sediment into the surrounding water.

Phosphorus solubilization in soil solution is currently understood to be driven mainly by chemical processes. An influential study by Mortimer (1941) demonstrated that P sorbs to iron III (ferric iron) in the presence of oxygen and is released under anaerobic conditions concomitantly with reduced iron II (ferrous iron). Patrick and Khalid (1974) expanded on Mortimer's (1941) idea, and found that reducing conditions also allow for more P uptake by the soil matrix in the presence of high soluble P concentrations, presumably because reduced iron is more reactive than ferric iron. Dillon and Molot (1997) found that SRP was related to dissolved organic carbon (DOC) and suggested this could be due to humic matter having a strong affinity for phosphate in the presence of iron. However, it is hard to translate these concepts into a predictive tool for P solubilzation. Many studies that attempted to use a ratio of soil P to available Fe and Al, termed P saturation, to predict soluble P in groundwater or runoff have produced mixed results (Shober and Sims 2009). For example, Davis et al. (2005) found that P saturation was significantly, although not strongly, related to SRP.

Moreover, researchers trying to link P solubility and runoff with land use and soil properties have achieved inconsistent results. Jones et al. (2001) found that landscape metrics such as percent urban or barran areas explained 73% of the variability in soluble phosphorus concentrations. However, Young and Briggs (2008) did not find a significant difference between shallow groundwater SRP concentrations in buffers and croplands, nor did they find that soil P was a reliable indication of SRP concentrations. Soldat et al. (2009) found that Morgan, Mehlich-3 and $CaCl_2$ extractable soil P concentrations at any depth were not accurate predictors of the amount of SRP that would be produced in overland runoff from turfgrass. Because turfgrass is the main type of pervious surface in urban and suburban areas, it is often considered to be a main source of urban P pollution.

An important conceptual idea now taking root in many estimates of soluble P loads is the idea that some areas are more hydrologically connected to streams and lakes than others, either by close proximity, or because they are connected through other frequently waterlogged, runoff generating areas of the landscape (Buczko and Kuchenbuch 2007). In humid, well vegetated regions, this implies that areas closest to surface water, either perennially or seasonally through variable-source-areas (VSAs) (Dunne and Leopold 1978) are the main drivers of P export. Thus, studies that focus on areas with a high propensity to saturate are important for understanding P solubility and export dynamics. Soil Topographic Indexes (STIs), which are a measure of an area's propensity to saturate, can be used in combination with P application dynamics to predict P export potential (Easton et al. 2009; Endreny and Wood 2003).

However, among areas that frequently water-saturate, there is a wide variety of soluble P dynamics that can occur, and our inability to predict the nature of P limits our ability to effectively manage SRP transport. Riparian buffers, which are often used to prevent nutrient (both nitrogen and phosphorus) transport to streams, are not consistently useful in preventing P transport (Walter et al. 2009). These areas can take the form of wetlands, uncultivated grasslands, or woodlands along surface water bodies, and are variably water-saturated. Many studies have shown that wetlands and other riparian areas are not predictable in their propensity to trap or export P. For example, Klotz (1997) found that beaver ponds could either increase or decrease downstream SRP concentrations depending on time of year and other unknown factors. Young and Briggs (2008) likewise did not find a statistically significant difference between groundwater SRP concentrations between riparian buffers and croplands.

The inconsistent success of these diverse strategies for predicting and preventing P solubilization and leaching indicates that further understanding of the processes involved in P solubilization and transport are important. Only recently have researchers begun to acknowledge the importance of biological processes in P desorption or solubalization. Stutter et al. (2009) found that natural areas near streams often become P sources and suggest that this could be caused by increased microbial and plant activity liberating soil-bound P. Likewise, Quang and Dufey (1995) found that the P–sorption capacity of soil iron was much greater at 30ºC than at 20ºC and conclude that this is due to microbial activity lowering the redox potential at the higher temperature. Furthermore, researchers have found that hydraulic variability such as flooding and drying of soils can significantly increase the availability of soluble P in laboratory studies (Banach et al. 2009; Turner and Haygarth 2001).

Our field study attempts to examine the intersection of hydrological and biological variability in three frequently saturated areas near an agricultural field in Harford, NY. We asked the questions: i) Are there overall differences between P solubility in VSAs experiencing different rates and degrees of saturation and desaturation? ii) How do the hydrological changes interact with seasonal changes to influence P solubility?

Study Site Characterization

We investigated three VSAs on Cornell University's Teaching and Research farm in Harford, NY. The first two sites, designated Dry Riparian (DR) and Wet Riparian (WR) respectively, were seasonally flooded areas next to an ephemeral stream at the base of a manure-fertilized alfalfa field. DR was further upstream than WR and tended to dry out more completely in the summer. According to the US NRCS soil database, both these sites had Wayland silt loam soils with a 0-2% slope. The third site, Upland Forested (UF), was a wooded upland site above the field, with Volusia channery silt loam soils at a 2-8% slope (Figure 1). The depth to the restrictive layer in the two lowland sites was approximately 200 cm, while the depth at the upland site was 40 cm (US Department of Agriculture, Natural Resources Conservation Service, 2006).

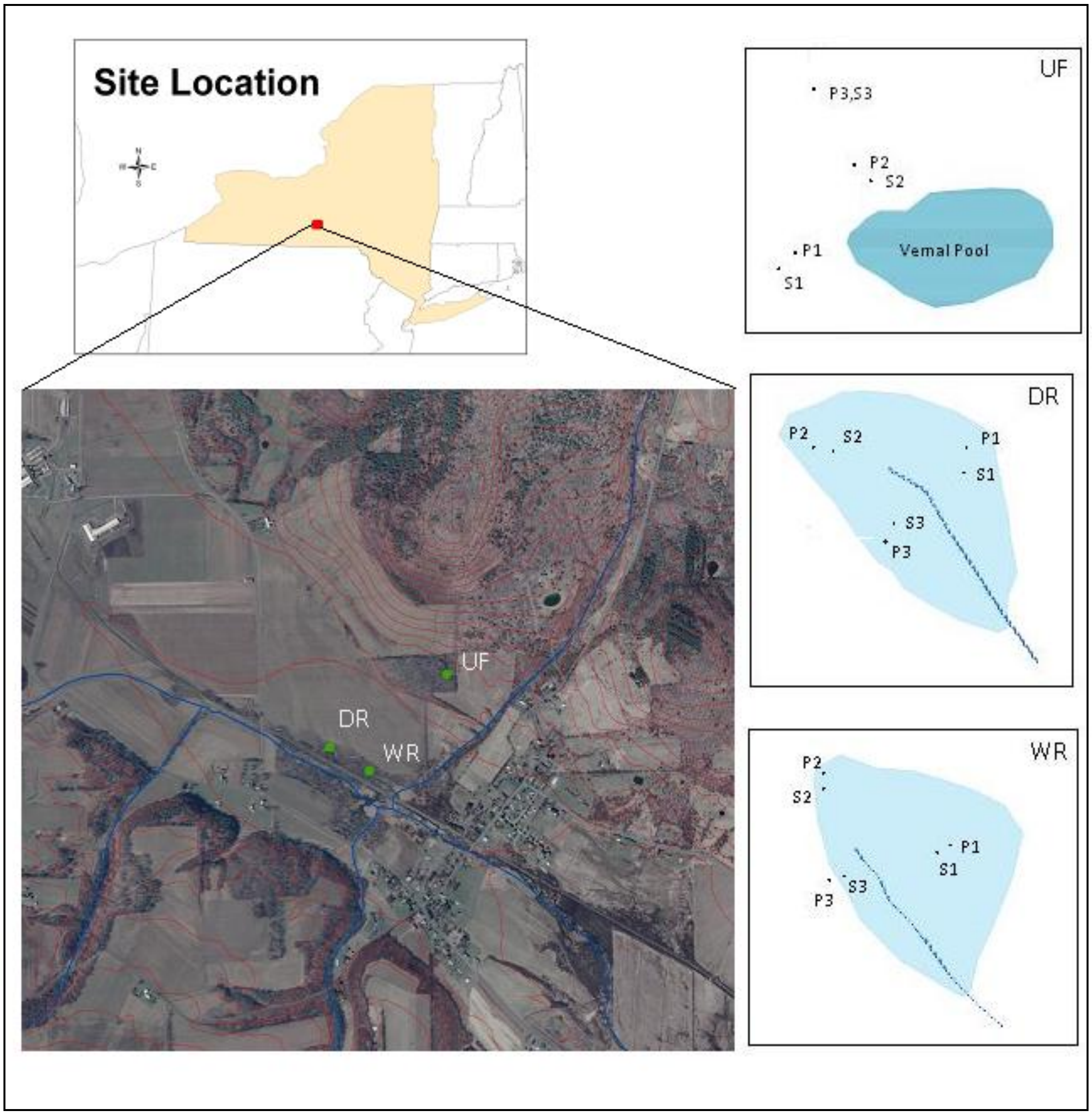


Figure 1: Location of sample sites and wells. Shaded region in UF represents a vernal pool, and the lighter shaded region in DR and WR represents the approximate maximum extent of the seasonally flooded area.

During the study year (September 2007 – August 2008), this area received 117 cm of precipitation, with no statistical difference in precipitation amount among seasons ($p=0.34$). Both riparian sites, DR and WR, were saturated for approximately 7 months of the year, during winter through early summer. The ephemeral stream in DR flowed for 6 months, from approximately January 2008 until June 2008. The stream in WR ran 9 months, approximately from November 2007 until August 2008.

The upland site was situated around a vernal pool in a wooded area just above the agricultural field bordering the riparian sites (Figure 1). This pool tended to fill and dry out on a shorter time scale than the ephemeral streams in the two lower sites, and was approximately associated with storm events. Manure was spread on the field above the two riparian sites on July 17, 2007, January 22 – February 15, 2008, and March 27, 2008.

CHAPTER 2

METHODS

Well Placement and Water Sampling

Each site had three shallow (depth of 50 cm or less) water sampling wells (S1-S3) and three shallow piezometer (water table monitoring) wells (P1–P3), except in the upland forested site, where well P3/S3 functioned both as a piezometer well and a sampling well. Depth to water table was measured using 50 cm Capacitance Water Level Probes (Odyssey Dataflow Systems) in three wells at each site. We found that these probes often malfunctioned, especially in winter, so when possible we interpolated between wells and time periods to get a more complete description of groundwater behavior. A well was considered water-saturated when the water level was above 10 cm below the soil surface, following Lyon et al.'s (2006) finding that runoff increases dramatically above this water table height.

Water was collected from each sampling well biweekly, when water was in the sampling well, from September 2007 until August 2008 for nutrient concentration analysis except when dry or frozen. Water samples were filtered on a 0.45 µm membrane filter within 2 hours of collection and stored at 4ºC until processing. Each date group of samples was analyzed with a method blank consisting of de-ionized water which was filtered, stored and analyzed with the samples to determine the detection limit of each analysis method. Any sample that read below the average of all blanks (the detection limit) for a particular nutrient was assigned a concentration of one half the detection limit.

The concentration of inorganic P, referred to here as soluble reactive phosphorus (SRP), was measured using ascorbic-acid reduction on an OI Analytical FS-3000 flow injection autoanalyzer within 48 hours of sample collection. During the course of the year, the detection limit for this methodology changed due to refinement of the technique. Therefore, all samples collected up until March 11, 2009 had a detection limit of 0.023 ppm. Those collected after this date had a detection limit of 0.017ppm.

Total P and Fe were analyzed using Inductively-Coupled Plasma Mass Spectrometry. The detection limits for these were 0.023 ppm and 0 .046 ppm respectively. These measurements were unable to be taken for samples in February 25 through April 3, 2008 (six sample dates), so our data set is missing iron, total soluble P and organic P data for these dates. We measured dissolved organic carbon in the water samples by persulfate oxidation on an OI Analytical TOC analyzer. Dissolved organic P was calculated as the difference between total soluble P and SRP.

Soil Collection and Analysis

Soil was collected after the water monitoring portion of the study was over, on June 1, 2009 from each site at two depths, 0-10cm and 10-20 cm. Because the upland site had substantially different water table behavior among the piezometer wells at this site, soil samples were taken from within 60 cm of the two extreme wells in UF, well P1 and well P3. Soil samples for the two riparian sites were composite samples of soil taken from near all sampling wells. The soil was taken back to the lab and air dried for a week before being ground and sieved through a 2 mm sieve. These samples were then analyzed for organic matter, Morgan extractable P, Fe, Al and HNO_3-extractible P, Fe, Al and total carbon at the Cornell Nutrient Analysis Laboratory. The Morgan extraction is a weaker extraction technique than the commonly used Mehlich 3 or Olsen tests, and is used to approximate the plant-available P in a soil (Ketterings and Barney 2006). Microwave assisted nitric acid digestion is used to dissolve the more tightly-bound nutrients in a soil, and can be used to approximate the total concentration of a nutrient in a soil.

Statistical Analysis

All statistical analysis was done with JMP 7.0 software (SAS Institute). Any analysis comparing behavior between sites was only done for sample dates when we had at least one water sample from each site. This meant that data from September 2007 were omitted from analysis when comparing between sites because wells in DR were dry at this time, and also data from January 2008 because frozen water in the upland site prevented sample collection at that time. Significance was assumed when $p < 0.05$.

CHAPTER 3

RESULTS

Hydrologic differences between sites

There was a marked difference in the rate of change in water table depth between UF and the two riparian sites (DR and WR). The upland site was characterized by rapid increases and decreases in depth to water table throughout the year, with changes of over 300 mm possible within a 24-hour period. These sharp changes occurred throughout the year after rainfall and/or snowmelt events. In contrast, the water levels in lowland sites remained relatively constant on a daily and weekly timescale, with one or two major seasonal increase and decrease in the year (Figure 2).

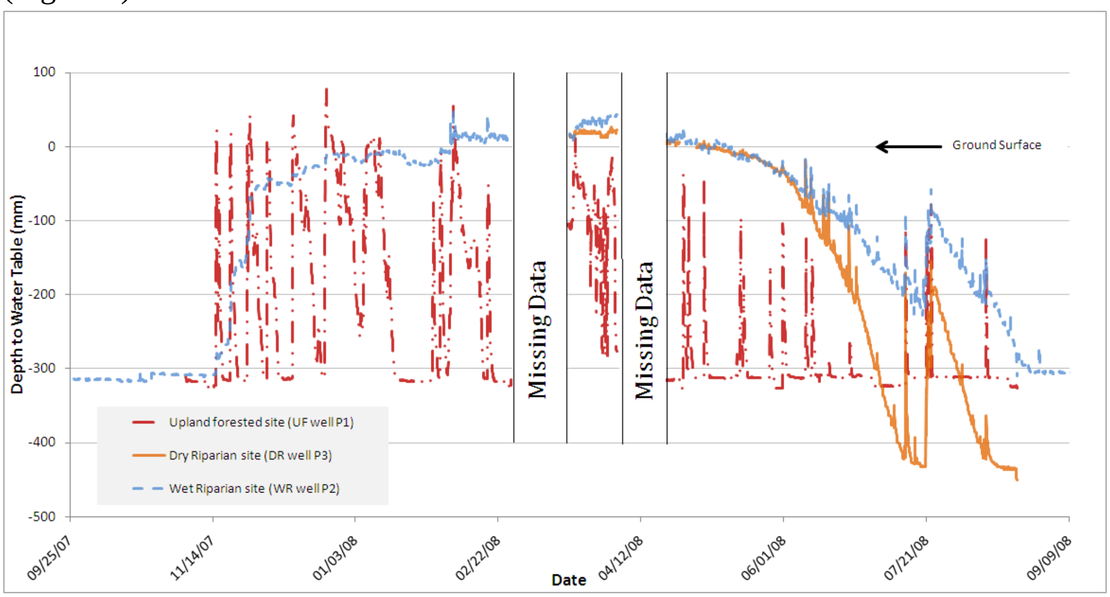


Figure 2: Depth to water table at one well from each site over the entire study period. Negative numbers are below ground surface, above zero indicates that the groundwater was above the land surface. Red: UF- P1, Orange: DR-P3, Blue: WR-P2.

The soil depth, saturated hydraulic conductivity and topography of the area were used to make a Soil Topographic Index (STI), Figure 3, which reflects the tendency of a 10m by 10m area of land to saturate, with higher numbers indicating a higher probability of water-saturation (Beven and Kirkby 1979).

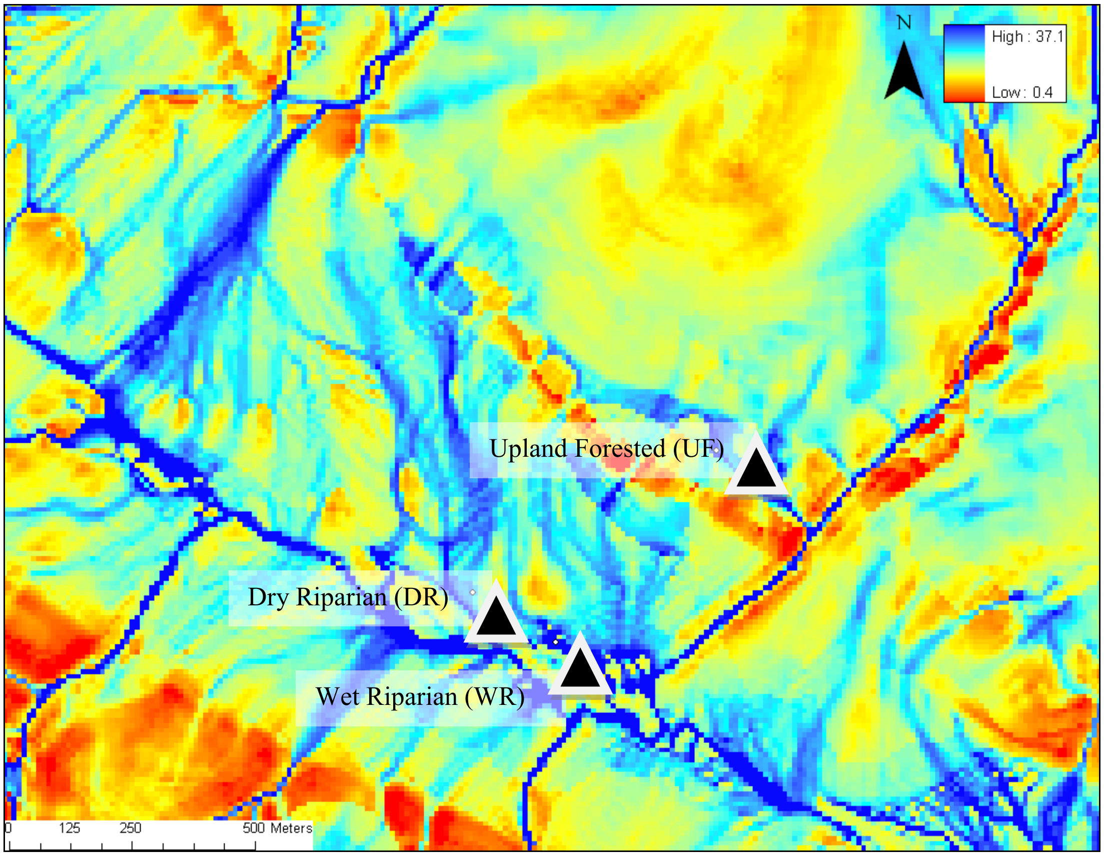


Figure 3: Soil Topographic Index (STI) of the field site in Harford, NY

Wells in DR, WR and UF had STI ranges of 9-11, 27-30, and 8-13 respectively (Table 1).

Table 1: Average nutrient concentrations, STI values and selected soil properties in the three sites. Soil from DR and WR were composite samples from near all three sampling wells. Soil from site UF was collected from near well S1 (the driest), and S3 (the most frequently saturated)

	WATER		**SOIL**			
Site	**Average total P, ppm (std. dev.)**	**Average SRP, ppm (std. dev.)**	**Average STI (range)**	**Soil depth**	**Morgan extr. P, mg/kg**	**Nitric Acid P, mg/kg**
DR	0.049 (0.051)	0.028 (0.019)	10.1 (9.3-10.9)	Top 10 cm 10-20cm	3.5 2	930 802
WR	0.050 (0.057)	0.028 (0.017)	27.9 (27.1-29.5)	Top 10 cm 10-20cm	5.5 4	874 823
UF S1	0.087 (0.079)	0.041 (0.016)	7.9	Top 10 cm 10-20cm	7 3.5	1638 1553
UF S3	0.110 (0.085)	0.058 (0.036)	12.9	Top 10 cm 10-20cm	7 2.5	1072 694

Although these STI values predict DR to be waterlogged for a shorter length of time than WR, we found both riparian areas were saturated for approximately 7 months of the year, from late November until late June, although DR tended to have a lower water table depth during the dry months. Both riparian sites were characterized by broadly uniform water table depths among wells within the same sites. In contrast, the difference in STI values at the upland site, UF, was much more predictive than in the riparian sites of the number of saturated days within a particular well. Within this site, well P1 (with a STI value of 7.9) frequently dried out during all seasons, while well P3 (STI 12.9) was rarely dry even at the end of the summer (Figure 4).

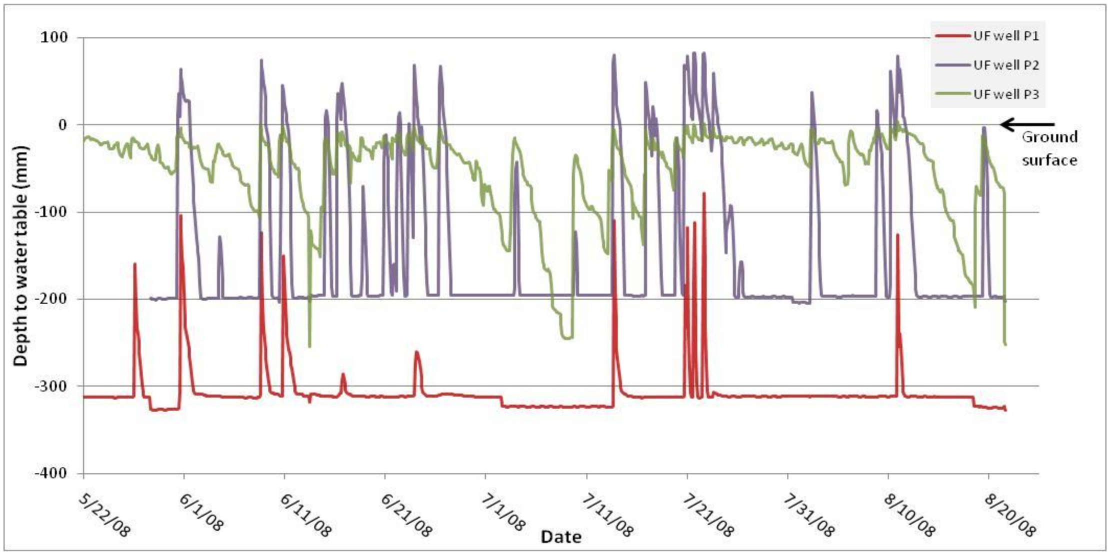


Figure 4: Groundwater heights among three wells within 20 m of each other in the Upland Forested Site during the summer of 2008 (Note – the horizontal sections at low values represent the lowest value measurable by the probe and the actual water levels could have dipped lower than this). Wells in the two riparian sites were much more uniform, correlating with other wells in the same site linearly with r^2>0.98 (excluding times when the depth of the water table was deeper than the bottom of the probe).

Nutrient Concentrations

The upland site had significantly higher SRP, total P, DOC and iron concentrations in shallow groundwater than the other sites (Figure 5). Soil Morgan extractable P and Fe and nitric acid digested P concentrations are reported in Table 1. Top 10 cm soil P concentrations, although higher in the upland site, were not useful in predicting SRP or total P concentrations in the shallow groundwater. For example, the ratio of Morgan-extractable P:SRP varied substantially among sites; this ratio was 135, 203,170 and 116 for DR, WR, UF-S1 and UF-S2, respectively.

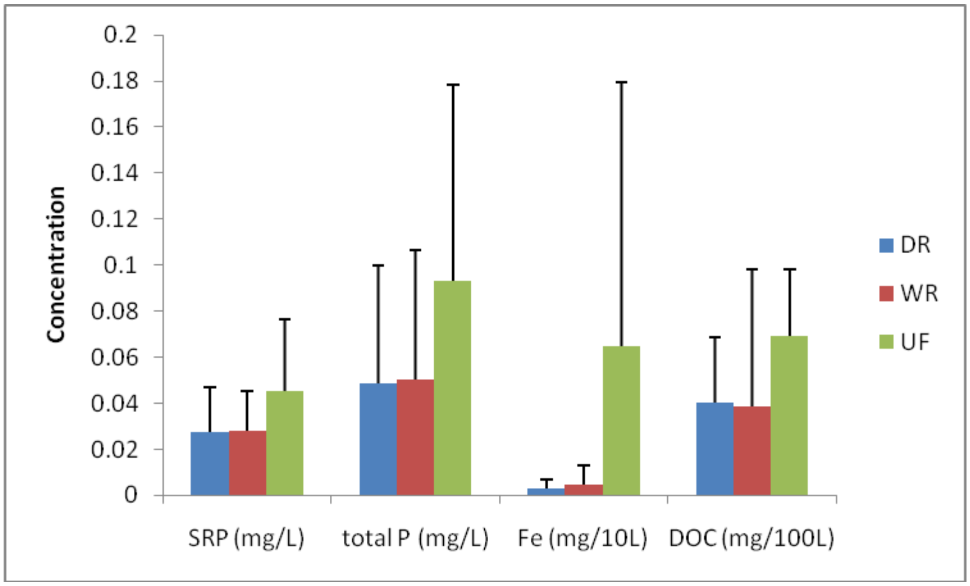


Figure 5: Comparison of nutrient concentrations between sites (note the different units between nutrients). Error bars represent one standard deviation from the mean. The upland forested site had significantly higher average concentrations of SRP ($p<0.0001$), total P ($p=0.0003$), Fe ($p<0.0001$) and DOC ($p<0.0001$) compared with the riparian sites.

Total P concentrations were weakly, but significantly positively, correlated with temperature ($R^2 = 0.08$, $p=0.0002$) (Figure 6a). This was driven by organic P, which was the fraction of P that was strongly related to temperature ($r^2=0.58$, $p<0.0001$) (Figure 6c). In contrast, SRP was not significantly correlated with temperature.

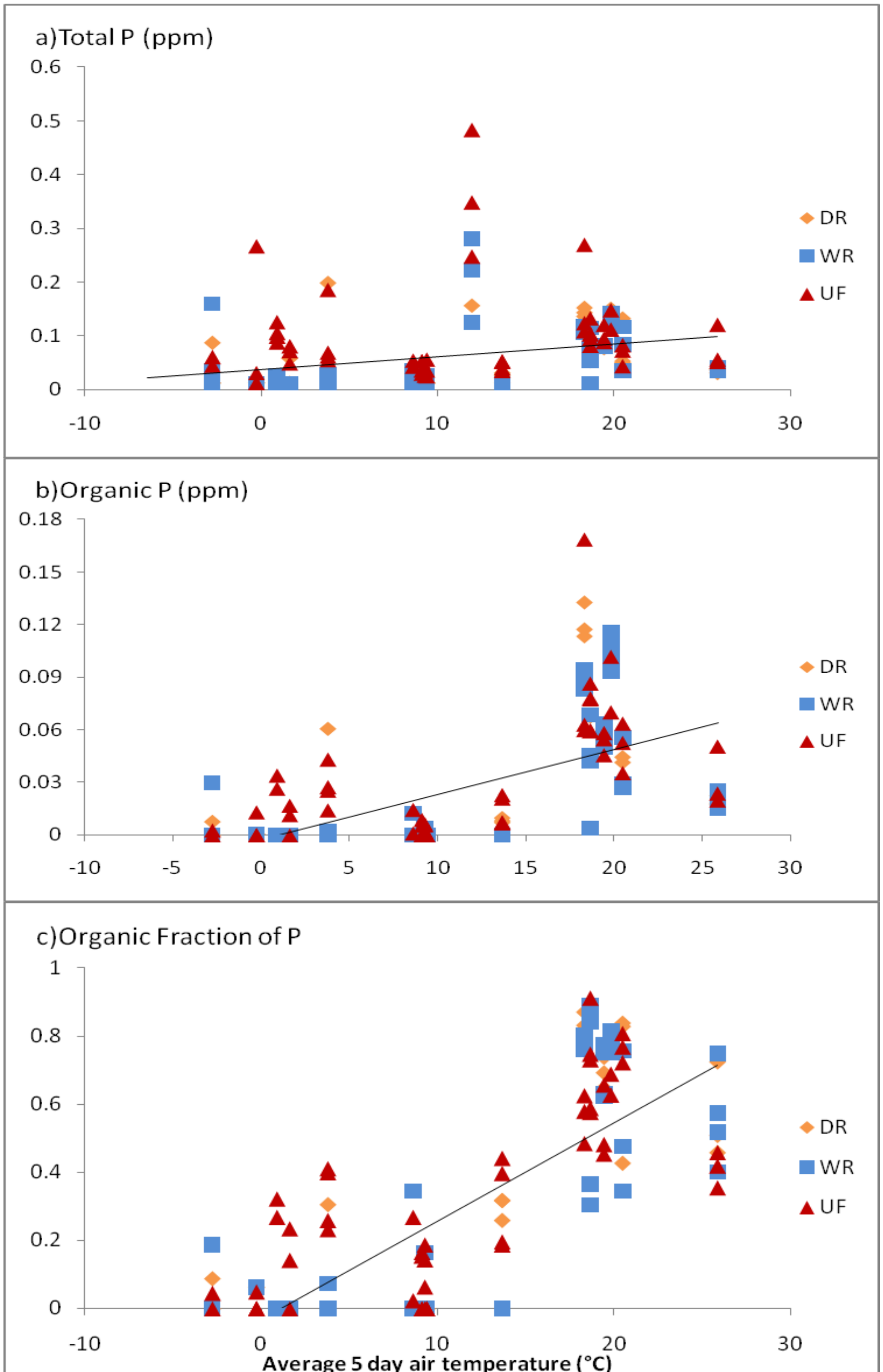


Figure 6: (a)Total P vs. temperature: $r^2 = 0.08$, p=0.0002; (b) Organic P vs. temperature: $r^2 = 0.37$; p<0.0001; (c) Organic P portion of total P: $r^2 = 0.59$, p<0.0001; There was no significant relationship between temperature and SRP

Divided by seasons, SRP was significantly highest in the fall, while organic P was highest in the summer (Figures 7). Manure application did not produce a noticeable increase in total P or SRP concentrations within a month following application, except in surface water samples on February 18, 2008, which followed a February 15 application.

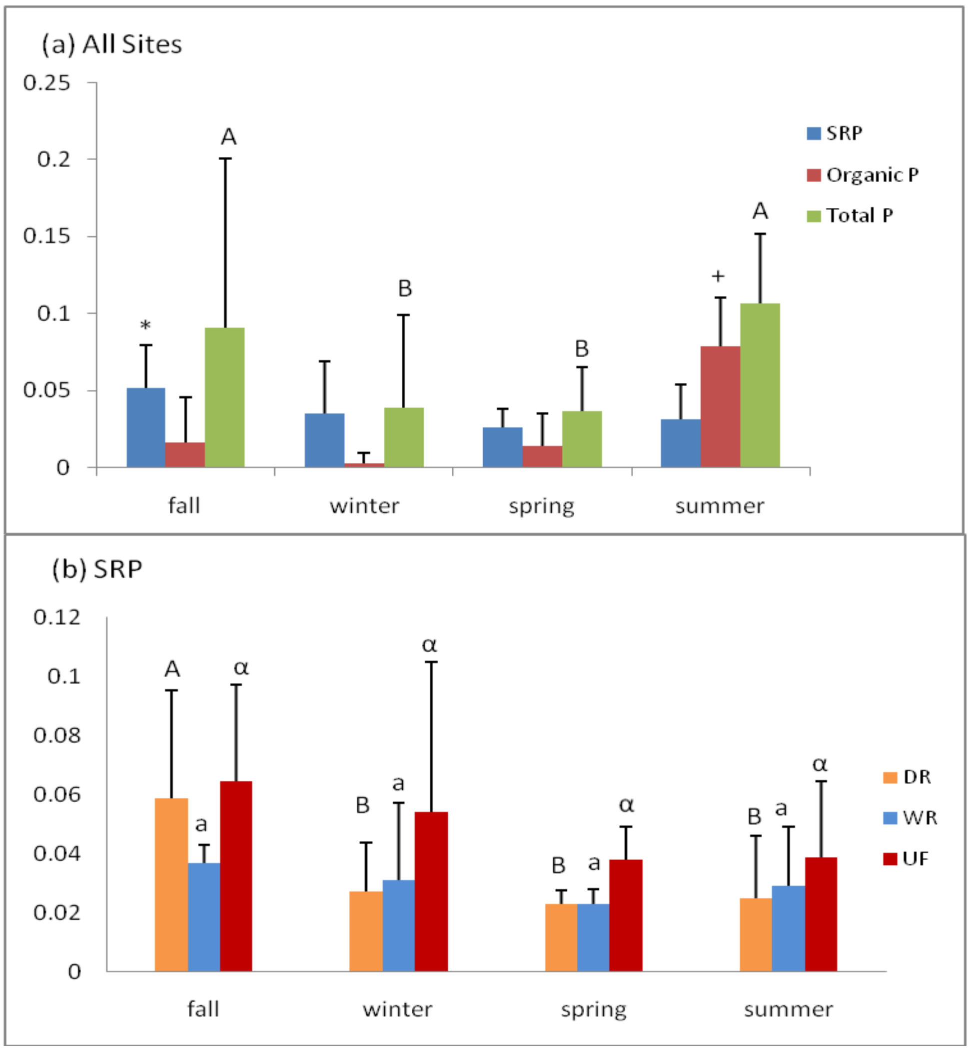
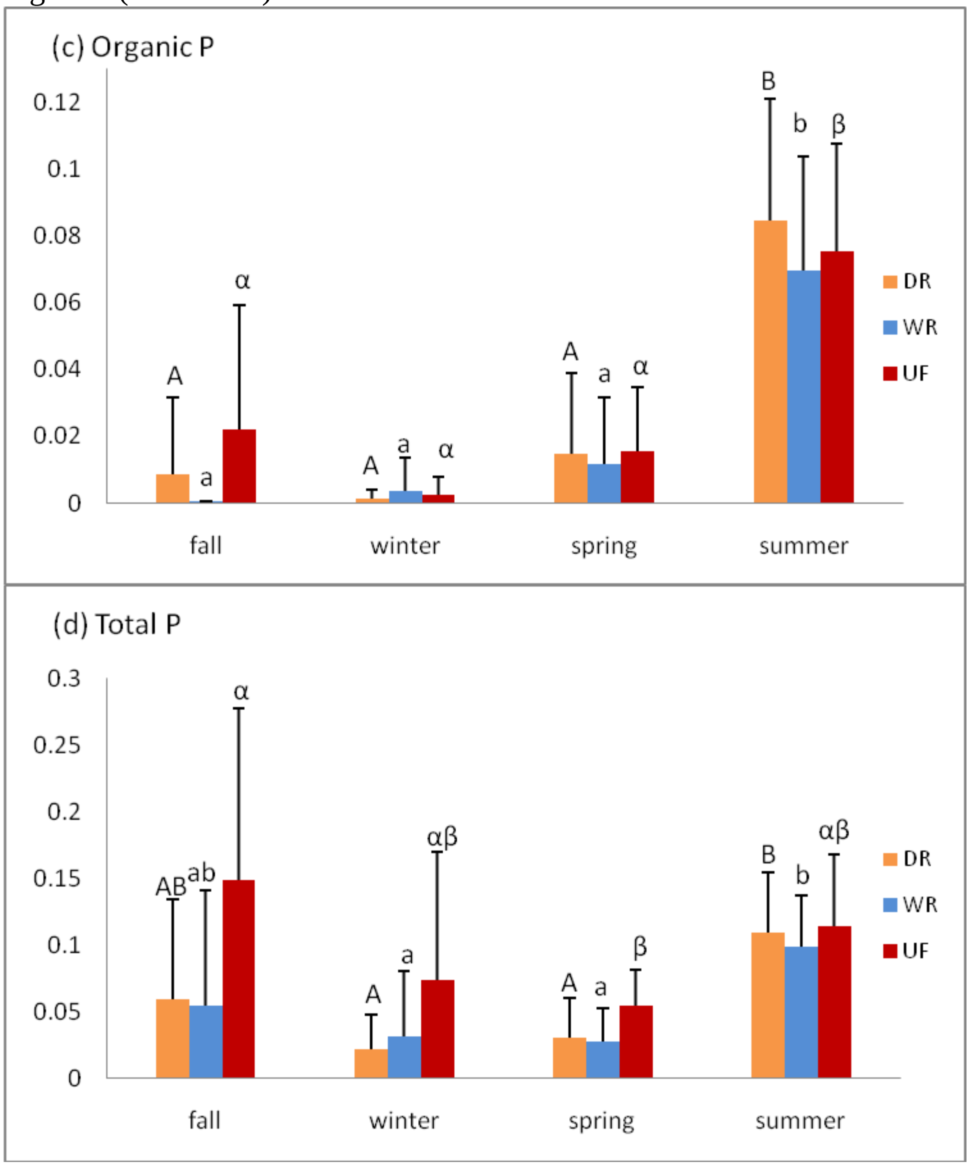


Figure 7: (a) Among all sites, the average concentration of SRP was significantly greater in the fall than in other seasons, as denoted by * ($p<0.0001$). Organic P concentrations were highest in summer, denoted by + ($p<0.0001$), and total phosphporus was highest in summer and fall ($p<0.0001$). Divided by sites: (b) SRP concentrations (c) Organic P (d) Total P. Among individual sites, significant differences were noted by letters, A/B in DR, a/b in WR, and α/β in UF; values without significant differences share a letter.

Figure 7 (Continued)



The two riparian sites had a significantly higher concentration of total and organic P, DOC and Fe under unsaturated conditions, but these differences were not seen in the upland forested site.

Iron was significantly correlated to SRP concentrations when all sites were considered together, $r^2 = 0.56$ (Figure 8). SRP concentrations were not related to Fe concentrations in the two riparian sites, but in the upland site there was a significant linear relationship between iron and SRP. Total P was weakly, but significantly, correlated in all three sites with Fe ($r^2<0.27$) (data not shown).

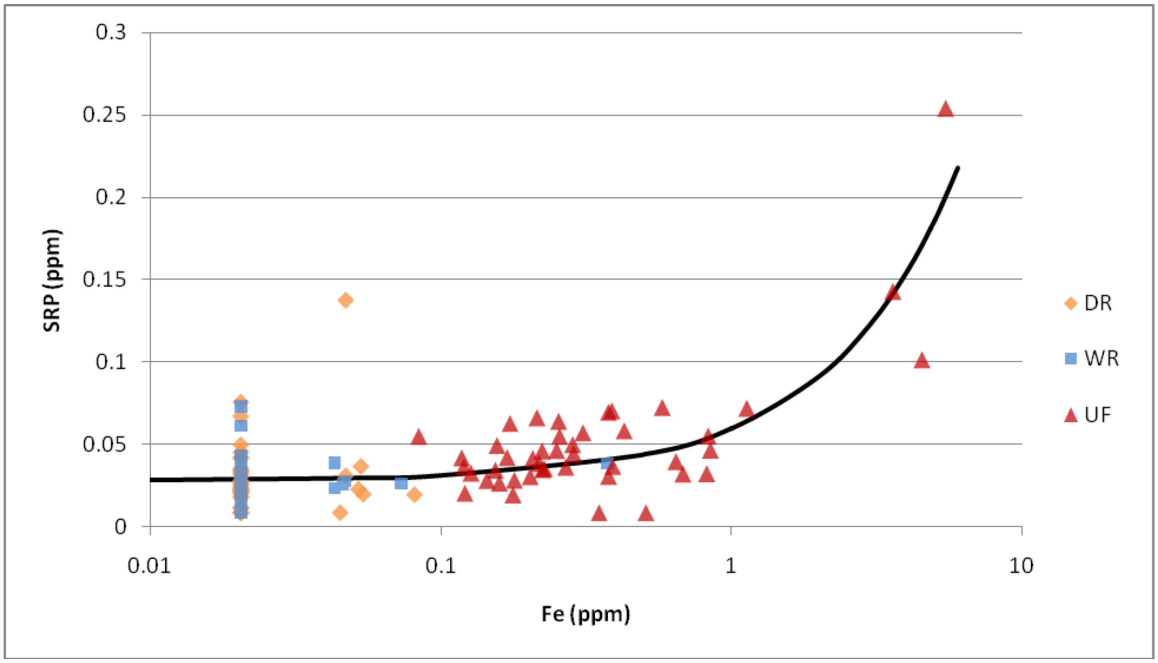


Figure 8: Groundwater SRP plotted against iron concentration. Diamonds =DR, squares =WR, triangles=UF. Solid curve represents best-fit linear relationship, $r^2=0.57$, $p<0.0001$. When examined individually, neither of the two riparian sites had a significant correlation between Fe and SRP, but the correlation between these nutrient concentrations in UF was high ($r^2=0.72$, $p<0.0001$)

CHAPTER 4

DISCUSSION

All the wells studied had STI values greater than 7, and all except one pair (UF S1,P1) had STI values greater than 9. In choosing these locations, we were hoping to capture the dissolved P dynamics in areas that we expect to water-saturate and contribute runoff frequently. Additionally, a high propensity to saturate would also drive redox reactions that have the potential to release Fe and P from the soil matrix. However, the STI, in describing an area's probability of water-saturating, does not capture the frequency saturation-desaturation cycles. Instead, we found that our upland site (UF) had a dramatically different pattern of wetting and drying compared to the lowland site with approximately the same STI range (DR).

The dramatic difference between upland hydrology and riparian areas is not surprising, as water in the upland soils would be expected to quickly drain to the lower areas, while riparian areas, with larger contributing areas and shallower slopes, remain waterlogged for a longer period of time. However, there is also a large difference in soil properties between the two landscapes, most significantly in Morgan-extractable Fe and P in the top 10 centimeters, and the soil depth. It is possible that the frequency of saturation-desaturation cycles could have caused the 5-100 fold higher concentrations of Morgan-extractable Fe in the upland site compared to the riparian areas and, therefore, it is difficult to decouple this dramatically different soil composition from the hydrology of the sites. Our research has shown that the upland site has both an increased rate of saturation and desaturation cycles and increased nutrient concentrations in the shallow groundwater. However, the exact mechanisms involved remain unclear.

Our results do not support the concept of using P saturation to determine a soil's ability to generate P in the shallow groundwater. Both Al and Fe concentrations were consistently higher in upland soils under both extractions techniques (Morgan and Nitric Acid). P saturation theory would expect these soils to have higher potential to adsorb P to the Fe and Al in the soil matrix, which was not seen in our results. In contrast the upland soil consistently had higher dissolved P in the shallow groundwater despite its apparent potential to form precipitates and complexes in the soil.

Previous research has suggested that water-saturated conditions could be expected to increase P concentrations in groundwater, due to low redox potential (Banach et al., 2009) and interaction of groundwater with the organic portion of the surface soil (Macrae et al., 2005). However, this was not the case in this study. Notably, we found the opposite to be true for the riparian sites for total and organic P (although not for SRP); where wells had lower concentrations of total P ($p<0.0001$ for both sites) and organic P ($p<0.001$ for both) when water-saturated than when unsaturated. Seasonal factors could be driving this relationship, as the driest periods in these two sites, summer and fall yield the highest P concentrations. Additionally, there was no such relationship in the upland site, where both saturated and unsaturated conditions occurred in all seasons.

Models used for prediction of P loads often will incorporate land use type in their design (e.g. Easton et al. 2009; van der Perk et al. 2007) in contributing to P pollution. However, this study lends support to the idea that it is landscape position, or drainability, that most strongly influences an area's ability to contribute dissolved P to surface waters. Indeed, it is our upland site, (which is forested - a land use type that is commonly associated with low P exports) that has the highest P concentrations in its shallow groundwater. Macrae et al. (2005) also found that upland soils had a higher concentration of water-extractable P, which correlates well with dissolved P in runoff, compared to lowland areas. Indeed, they found that this correlation was stronger for landscape position than for type of forest use (harvested vs. unharvested forest).

The seasonality of dissolved P in the shallow groundwater is in direct contrast to nitrogen concentrations, which are highest in winter and lowest in summer due to uptake by plants and soil biota. Although P is also an important nutrient for all organisms, we do not see a similar net uptake of P in the growing seasons. Our results show that over all sites, SRP was highest in the fall, while organic P peaked in the summer, although the data had significant scatter within and among dates. Divided by sites, these general patterns hold; however, UF did not have a significant difference in SRP between seasons. In contrast, Scott et al. (2001) found that SRP concentrations in runoff from a forested catchment were highest in late spring and early summer, with a clear increasing trend throughout spring, peaking in summer. While our results do not have such a neat or early peak (see Figure 9), the difference could be explained as a difference in runoff versus. groundwater. Concentrations were highest in summer and fall (these corresponded to the driest months) so it is possible that the actual loads to receiving surface waters were highest in late spring when the water table was high and concentrations were starting to increase.

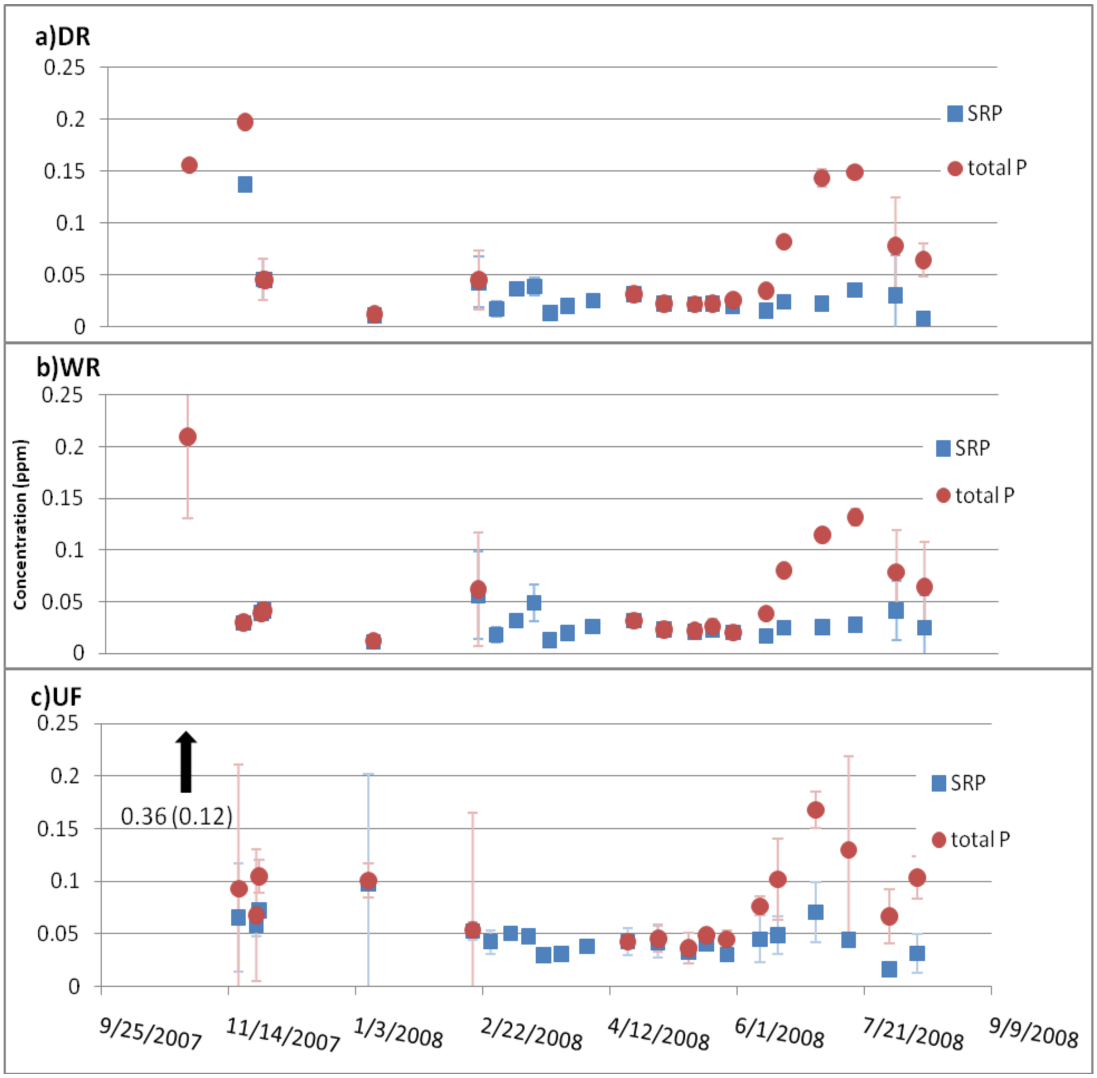


Figure 9: Average concentration of SRP (squares) and total P (circles) by date over the course of the study year in (a) DR, (b) WR and (c) UF water samples. On 10/27/09, the average total P concentration of water samples from UF is off the scale, with a values of 0.36 and a standard deviation of 0.12 (SRP concentration not measured on this date). Error bars represent one standard deviation from the mean.

Additionally, it is possible that our measurements of high P concentrations in the riparian sites during the fall are related to a mid-July 2007 spreading of manure. Manure spreading did not seem to affect P concentrations when spread during our study period during the winter. Before the study was initiated manure had been applied mid-summer, when biological activity was at its peak. It is possible that some of the P became bound in organic matter during this time, and was then slowly released through the following fall. Grab samples taken from these sites in the fall following the study period did not show similarly high concentrations of SRP or total P, and no manure had been spread that summer.

Because of the strong seasonality in our results, as well as a weak but significant relationship between P concentrations and temperature, it appears that biological mobilization is important to the release of P from the soil matrix and/or the biomass of an area. In the lowland sites, where seasonality was strongest for SRP, SRP increased slightly in mid-spring before dipping again in late spring and early summer when organic P concentrations greatly increased (Figure 9). This suggests that plants and/or microbes were mobilizing SRP from the soil matrix in preparation for growth, converting the inorganic P to organic P. Such an early increase in organic P in the summer indicates either a dominance of the process by microbes, which have a faster turnover rate, or a secretion of P-containing compounds by plants.

In the upland site it is harder to see any patterns or seasonal trends. This might be explained by the more extreme changes in water table height creating a radically different microbial ecosystem from the lowland site, less driven by seasonal influences.

Preliminary PCR results using probes specific to Geobacter, an important family of iron reducers, has shown that these organisms are consistently present in soil and water samples taken from the upland site, while samples from the riparian sites do not show a consistent presence of these organisms (data not shown). Because organisms involved in iron reduction would be expected to release iron-bound P at the same time, a large population of these organisms might have an important impact on the effect of saturation and desaturation cycles in the field, especially in the upland site.

Additionally, in all three sites, we have PCR evidence of polyphosphate accumulating organisms (PAOs), which are the organisms responsible for P removal in Enhanced Biological Phosphorus Removal in wastewater treatment, and only recently have been considered in natural environments (Kunin et al. 2008; Peterson et al. 2008; Valdivia 2009). Although we do not know the relative abundance or significance yet of these organisms, their strategy of accumulating high amounts of P in aerobic periods and releasing this P in anaerobic periods would be expected to be more important in an environment where the cycling from anaerobic to aerobic conditions is fairly rapid, on the course of days (as in the upland site), as opposed to seasonally (in the two riparian sites).

It appears that not only is landscape position an important factor in P solubility in soils, but the controlling processes may differ according soil, hydrologic, and vegetation conditions. Developing a coherent framework to predict P mobilization remains a challenge.

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